

PATENT SPECIFICATION

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(54) EXPANDABLE POLYMERS OF VINYL(IDENE) AROMATIC COMPOUNDS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organized under the laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to expandable polymers of vinylidene aromatic compounds in the form of coated particles and to a process for the manufacture of these coated particles.

The manufacture of cellular moulded blocks or articles from expandable particles is well-known and involves essentially two steps, (a) pre-expansion of the expandable particles followed by a maturing stage and (b) heating the pre-expanded particles in a mould to form a cellular structure therein. For ease of handling and in order to obtain satisfactory mouldings it is desirable that the particles are free-flowing and that their tendency to agglomerate before, during and after pre-expansion is avoided as far as possible.

The Applicants have found a satisfactory coating composition for application to the expandable particles which not only largely prevents agglomeration of the expandable particles but also enables a reduction to be made in the mould cooling time. A moulding cannot be removed immediately from its mould because the cellular structure has to undergo equilibration with the atmosphere and any reduction in this period of equilibration known as the mould cooling time, is of considerable economic importance.

The present invention provides coated expandable particles of a polymer of a vinylidene aromatic compound with a coating composition comprising a glyceryl C₁₆—C₂₀ carboxylate and a metal stearate.

The glyceryl carboxylate may be derived from any monocarboxylic acid containing 16—20 carbon atoms. For economic reasons it is preferred to use a stearate as the glyceryl carboxylate because stearic acid is a readily available naturally occurring material. The carboxylate may be a mono, di- or tri-ester or mixture of these esters. Particularly preferred are the glyceryl mono-esters, for example glyceryl monostearate. A commercially available form of glyceryl monostearate is "Empilan" GMS—obtainable from Albright & Wilson Ltd which is said to contain at least 30 or 40% of glyceryl monostearate, the balance being the di- and tri-stearates and some free glycerol. The carboxylate may be present in the coating in an amount in the range of from 0.01 to 1.0% by weight of the expandable particles, preferably in the range of from 0.2 to 0.7% by weight.

The metal stearate may be water-soluble or water-insoluble. The water-soluble stearates, for example, sodium or potassium stearate, give a definite improvement to the flow characteristics of the pre-expanded particles but the improvement is more marked when a water-insoluble stearate is employed, for example, calcium or zinc stearate. If desired, a mixture of water-soluble and water-insoluble stearates may be employed, for example a mixture of sodium and zinc stearate. The metal stearate may be present in the coating in an amount in the range of from 0.005 to 0.1% by weight based on the expandable particles.

An advantage of the glyceryl carboxylate/

ERRATUM

SPECIFICATION No. 1,409,285

Page 1, Heading, below (52) insert (72)
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The present invention relates to expandable polymers of vinylidene aromatic compounds in the form of coated particles and to a process for the manufacture of these coated particles.

The manufacture of cellular moulded blocks or articles from expandable particles is well-known and involves essentially two steps, (a) pre-expansion of the expandable particles followed by a maturing stage and (b) heating the pre-expanded particles in a mould to form a cellular structure therein. For ease of handling and in order to obtain satisfactory mouldings it is desirable that the particles are free-flowing and that their tendency to agglomerate before, during and after pre-expansion is avoided as far as possible.

The Applicants have found a satisfactory coating composition for application to the expandable particles which not only largely prevents agglomeration of the expandable particles but also enables a reduction to be made in the mould cooling time. A moulding cannot be removed immediately from its mould because the cellular structure has to undergo equilibration with the atmosphere and any reduction in this period of equilibration known as the mould cooling time, is of considerable economic importance.

The present invention provides coated expandable particles of a polymer of a vinylidene aromatic compound wherein the coating comprises (a) a glyceryl C₁₆—C₂₀ carboxylate and (b) a metal stearate.

The invention also provides a process for the manufacture of the coated expandable particles of a polymer of a vinylidene aromatic compound, which comprises contacting ex-

pandable particles of a polymer of a vinylidene aromatic compound with a coating composition comprising a glyceryl C₁₆—C₂₀ carboxylate and a metal stearate.

The glyceryl carboxylate may be derived from any monocarboxylic acid containing 16—20 carbon atoms. For economic reasons it is preferred to use a stearate as the glyceryl carboxylate because stearic acid is a readily available naturally occurring material. The carboxylate may be a mono, di- or tri-ester or mixture of these esters. Particularly preferred are the glyceryl mono-esters, for example glyceryl monostearate. A commercially available form of glyceryl monostearate is "Empilan[®] GMS"—obtainable from Albright & Wilson Ltd which is said to contain at least 30 or 40% of glyceryl monostearate, the balance being the di- and tri-stearates and some free glycerol. The carboxylate may be present in the coating in an amount in the range of from 0.01 to 1.0% by weight of the expandable particles, preferably in the range of from 0.2 to 0.7% by weight.

The metal stearate may be water-soluble or water-insoluble. The water-soluble stearates, for example, sodium or potassium stearate, give a definite improvement to the flow characteristics of the pre-expanded particles but the improvement is more marked when a water-insoluble stearate is employed, for example, calcium or zinc stearate. If desired, a mixture of water-soluble and water-insoluble stearates may be employed, for example a mixture of sodium and zinc stearate. The metal stearate may be present in the coating in an amount in the range of from 0.005 to 0.1% by weight based on the expandable particles.

An advantage of the glyceryl carboxylate/metal stearate coating is that it can be applied to the expandable particles by a dry-coating route and thereby avoid the expense and hazard of using solvents or non-aqueous liquids as media from which the composition

* regd. Trade Mark

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is coated on the particles. However, if desired, the coating can be applied from a solvent or non-aqueous liquid without effecting the properties of the resulting coated particles.

The term "polymer of a vinylidene aromatic compound" as used in this specification includes homopolymers of vinyl aromatic and vinylidene aromatic compounds and copolymers of such compounds with other olefinically unsaturated monomers. Examples of vinylidene aromatic compounds are styrene, alpha-methyl styrene, the vinyl toluenes, and the halogen-substituted styrenes. For economic reasons the preferred polymer is homopolystyrene, and although the invention is not restricted to polystyrene, the description will hereafter refer to polystyrene for the sake of convenience.

As is well known expandable polystyrene particles contain a vaporisable expanding agent which causes the particles to expand or foam when heat or steam is applied to them. The expanding agent may be any material which has a boiling point or boiling range under atmospheric pressure below 100°C, and which has substantially no solvent action on the polystyrene. Examples of expanding agents are saturated aliphatic or cycloaliphatic hydrocarbons having 3 to carbon atoms, e.g., propane, butane, pentane and cyclohexane or halogenated hydrocarbons having 1 to 6 carbon atoms, e.g., fluorinated hydrocarbons, or other materials such as petroleum ether. The amount of expanding agent present in the particles should be sufficient to produce a cellular mass, but generally speaking should be present to the extent of 2–20% by weight based on the polymer.

The expandable particles are conveniently manufactured in the form of beads or pearls by suspension or emulsion polymerization of the vinyl(idene) aromatic compound, the expanding agent such as pentane or a pentane/isopentane mixture being incorporated therein during or after polymerization.

The coating composition may be applied to the expandable particles by any convenient technique. The ingredients may be applied separately or together and in any order. However, it is most convenient to apply them together and dry-coat the mixture on the expandable particles. If desired, the composition can be applied as a slurry or a solution in a readily vaporisable non-aqueous liquid which has no solvent action on the expandable particles, e.g., a lower alcohol such as methanol, ethanol, isopropanol or an aliphatic hydrocarbon, such as hexane, heptane or petroleum ether.

The coated expandable particles according

to the invention readily undergo pre-expansion and moulding procedures without clogging or otherwise interfering with the handling equipment which transfers pre-expanded beads to the mould. Flow of the raw bead, i.e., before pre-expansion, is also excellent and causes no difficulty. The coating agent employed increases the production from a given mould by reducing the mould cooling time and, also, surprisingly has no deleterious effect on the strength of the moulded articles.

The invention will now be illustrated by the following examples.

EXAMPLES I to III

Expandable polystyrene beads (97.25% of whose diameters lay between 350 and 850 microns) and containing about 6% by weight of a mixture of n-pentane and iso-pentane were tumbled in a ribbon blender with a dry coating composition consisting of a glyceryl monostearate and a series of metal stearates, the details of which are given in the Table appearing below.

The coated beads were pre-expanded in a continuous pre-expander using a steam/air mixture to give beads having a bulk density of about 25 kg/m³. The degree of bead agglomeration expressed as a percentage of the total beads was noted and is given in the Table for each example. The pre-expanded beads were allowed to mature overnight and were machine-moulded into plaques 1 foot by 1 foot 6 inches by 1 inch in a steam-heated enclosed mould in accordance with conventional practice. The mould cooling time (i.e., the time taken for the plaque to equilibrate with the atmosphere to enable it to be removed from the mould without distortion) was noted.

Two commercial grades of glyceryl monostearate were used: "Empilan® GMS" and "Empilan® GMS. SE", both of which are available from Albright & Wilson Ltd. The former (referred to as GMS in the Table) contains at least 30% by weight of glyceryl monostearate, the balance being glyceryl di- and tri-stearates and a small quantity of free glycerol (about 7% by weight). The latter (referred to as GMS.SE in the Table) contains at least 40% by weight of glyceryl monostearate, the balance being glyceryl di- and tri-stearates, a small quantity of free glycerol (about 7% by weight) and 6% by weight of sodium stearate.

For comparative purposes beads coated with glyceryl monostearate alone were subjected to the procedure outlined above and the result of this comparative run is given in the Table under the heading "Control".

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TABLE

Example	Coating agent (%wt on beads)	% Agglomeration	Cooling time
Control	GMS 0.5%	3.6	56 secs.
I	GMS.SE ^(*) 0.5%	1.2	48 secs.
II	GMS 0.5% + zinc stearate 0.02%	0.9	48 secs.
III	GMS.SE ^(*) 0.5% + zinc stearate 0.02%	0.5	48 secs.

10 ^(*) this product includes 6% (i.e., 0.03% by weight of beads) of sodium stearate.

15 It will be seen from the Table that the presence of a metal stearate in the coating composition gives a considerable reduction in mould cooling time. The natural tendency of the pre-expanded beads to agglomerate is also greatly reduced by the presence of a metal stearate, particularly zinc stearate, in the coating of the beads.

WHAT WE CLAIM IS:—

- 20 1. Coated expandable particles of a polymer of a vinyl(idene) aromatic compound, in which the coating comprises (a) a glyceryl C₁₆ to C₂₀ carboxylate and (b) a metal stearate.
- 25 2. Coated expandable particles as claimed in claim 1, in which the glyceryl carboxylate is derived from a monocarboxylic acid containing 16—20 carbon atoms.
- 30 3. Coated expandable particles as claimed in claim 2, in which the glyceryl carboxylate is derived from stearic acid.
- 35 4. Coated expandable particles as claimed in any one of the preceding claims, in which the glyceryl carboxylate is present in the coating in an amount in the range of from 0.01 to 1.0% by weight of the expandable particles.
- 40 5. Coated expandable particles as claimed in claim 4, in which the glyceryl carboxylate is present in the range of from 0.2 to 0.7% by weight of the expandable particles.
- 45 6. Coated expandable particles as claimed in any one of the preceding claims, in which the metal stearate is a water-soluble stearate.
- 50 7. Coated expandable particles as claimed in claim 6, in which the water-soluble stearate is sodium or potassium stearate.
8. Coated expandable particles as claimed in any one of claims 1 to 5, in which the metal stearate is a water-insoluble stearate.
9. Coated expandable particles as claimed in claim 8, in which the water-insoluble stearate is calcium or zinc stearate.
10. Coated expandable particles as claimed

in any one of the preceding claims, in which the metal stearate is present in the coating in an amount in the range of from 0.005 to 0.1% by weight based on the expandable particles.

11. Coated expandable particles as claimed in any one of the preceding claims, in which the polymer of a vinyl(idene) aromatic compound is a homopolymer.

12. Coated expandable particles as claimed in claim 11, in which the homo-polymer is homopolystyrene.

13. A process for the manufacture of coated expandable particles of a polymer of a vinyl(idene) aromatic compound which comprises contacting expandable particles of a polymer of a vinyl(idene) aromatic compound with a coating composition comprising a glyceryl C₁₆ to C₂₀ carboxylate and a metal stearate.

14. A process for the manufacture of coated expandable particles as claimed in claim 13, in which the components of the coating composition are applied separately to the expandable particles.

15. A process for the manufacture of coated expandable particles as claimed in claim 13 or 14, in which the components of the coating composition are applied together and the mixture dry-coated on to the expandable particles.

16. Coated expandable particles as claimed in claim 1, substantially as hereinbefore described with particular reference to Example I, II or III.

17. A process for the manufacture of coated expandable particles as claimed in claim 13, substantially as hereinbefore described with particular reference to Example I, II or III.

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